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SYNTHESIS OF RENEWABLE DIESEL FROM PALM OIL AND JATROPHA CURCAS OIL THROUGH HYDRODEOXYGENATION USING NiMo/ZAL

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ABSTRACT

Hydrodeoxygenation of palm oil and Jatropha curcas oil over NiMo/ZAL (nickel molybdenum/zeolit alam Lampung) catalyst was investigated under temperatures of 375°C and 400°C and H_2 pressure of 15 bar in a semibatch stirred autoclave reactor. NiMo/ZAL catalyst was prepared using a rapid cooling method. NiMo/ZAL characterization revealed a crystal size of 70.07 nm, surface area of 12.25 m^2/g, and pore size and pore volume of 9.83 Å and 0.0062 cm^3/g, respectively. The hydrodeoxygenation removal pathway of palm oil and Jatropha curcas oil over NiMo/ZAL catalyst was primarily achieved through decarboxylation. Under hydrogen pressure of 15 bar and temperature of 375°C, palm oil and Jatropha curcas oil can be converted into paraffin chains (from n-C_{15} up to n-C_{18}) by a decarboxylation reaction that produces water, methane, and CO_x gases as byproducts and contains some undesirable reactions. These byproducts can produce alkene bonds that form chains different from those in conventional diesel fuel. The conversion was 80.87%, selectivity was 52.78%, and yield was 45.66%. The hydrodeoxygenation reaction catalyzed by NiMo/ZAL catalyst was found to be suitable for removing oxygen and producing paraffin chains; this increased the heating value and stability of renewable diesel fuel.

Keywords: Hydrodeoxygenation; Jatropha curcas oil; NiMo/ZAL; Palm oil; Renewable diesel

1. INTRODUCTION

The biofuels industry is growing rapidly as a result of high petroleum prices and increasing concerns about global climate change. Currently, the primary route for producing diesel engine biofuels is the transesterification of vegetable oils (Demirbas, 2007). However, biodiesel has high viscosity, cloud point, pour point, nitrogen oxides (NO_x) emissions, and injector/engine wear and low energy density (Knothe, 2008). In particular, several routes have been tried for reducing the viscosity, such as diluting vegetable oils with diesel fuel, microemulsification with alcohols, pyrolysis, and transesterification (Scwab et al., 1987).

In recent years, a new reaction pathway called hydrodeoxygenation has been proposed to produce better biodiesel. Hydrodeoxygenation is a type of hydroprocessing in which oxygen is removed from an oxygen-containing compound under high pressure in hydrogen atmosphere at high temperature with the help of a catalyst. The liquid hydrocarbon products obtained from

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hydrodeoxygenation is called renewable diesel. Hydrodeoxygenation includes many other reactions such as hydrogenation, cracking, decarbonylation, and decarboxylation. In hydrogenation, the C-O bond is broken using H_2 gas, the carboxylic functional group is separated to form CO_2 by decarboxylation, and CO and H_2O are released through decarbonylation (Lestari et al., 2010; Boyás et al., 2012).

Renewable diesel can be produced through hydrodeoxygenation from many types of vegetable oil without compromising the fuel quality. Existing farm-based feedstocks such as rapeseed, sunflower, soybean oil, and even palm oil can be used for this purpose. However, as these feedstocks are also used for producing food, alternative nonfood oils such as Jatropha must be made available in the future in large, cost-effective volumes to substitute for a significant portion of fossil-based diesels. Jatropha curcas is a small or large shrub tree that produces nonedible seeds containing 30–40% oil, and it is considered ideal for renewable diesel production. Because Jatropha curcas plants are nonedible and grown in marginal, nonagricultural areas, require little water for cultivation, and do not compete with existing agricultural resources, growers can produce a volume of plants irrespective of rising food prices. Jatropha is now emerging as one of the prime contenders for biofuel feedstock supply for the years ahead (Silitonga et al., 2011).

Previous research showed that unsaturated fatty acids such as oleic and linoleic acids have to be hydrogenated first before hydrodeoxygenation can be conducted (Susanto et al., 2014). A catalyst is used to reduce the activation energy of this reaction and increase its selectivity. Metal or metal sulfide catalysts and pressurized hydrogen are useful for inducing the saturation of unsaturated carbon chains in triglycerides. Recently, Morgan et al. (2010) reported the catalytic deoxygenation of triglycerides such as tristearin, triolein and soybean oil over Ni, Pd, and Pt metals. Their results indicated that Ni shows higher catalytic activity for the deoxygenation of triglycerides and cracking of fatty acids compared to Pd and Pt. In this study, the hydrodeoxygenation of palm oil and Jatropha curcas oil over NiMo/ZAL catalyst synthesized through a rapid cooling method in a semibatch stirred autoclave was demonstrated.

2. EXPERIMENTAL SETUP

2.1. Materials

The following chemicals were commercially available and used as received: palm oil RBDPO, Jatropha curcas oil (IPB, Bogor), nickel nitrate hydrate Ni $(NO_3)_2.9H_2O$ and ammonium heptamolybdate tetrahydrate $(NH_4)_6.Mo_7.O_{24}.4H_2O$ (Merck), natural zeolite from Lampung ZAL (Clinoptilolite type, CV Minamata), and polyethylene glycol (PEG, MW20,000; Merck).

2.2. Catalyst Preparation

NiMo/ZAL catalyst with Ni and Mo loading of 5% and 20%, respectively, were prepared by a rapid cooling method in a PEG solution. Metal nitrates were used as the precursor in this preparation. Metal nitrates from each compound were dissolved in aquadest, and ZAL was slowly poured into this solution. Then, the solution was mixed with PEG 20,000, stirred, and heated until the PEG dissolved completely. The solution was heated until the water in it vaporized or the precursor solution turned into a gel. The gel precursor was calcined at 600°C for 30 min to remove the nitrates and PEG and then cooled rapidly to ambient temperature in 60 min.

2.3. Catalyst Characterization

The catalysts were characterized by Autosorb-6B BET to determine the area, pore size, and pore volume; X-ray diffraction (XRD) to determine the nature and type of crystal catalyst; and SEM-EDX (JED-2300 Analysis Station JEOL) to determine the morphology and composition.

2.4. Hydrodeoxygenation of Palm Oil and Jatropha Curcas Oil

Palm oil and Jatropha curcas oil were hydrodeoxygenated in a 250-mL semibatch stirred autoclave reactor. The feed:NiMo/ZAL catalyst ratio was 100:1. The reactions were performed at a temperature of 375°C and H_2 pressure of 15 bar in a semibatch stirred autoclave reactor. Every 15 min, the resulting gas was analyzed online by gas chromatography with a thermal conductivity detector (GC-TCD) with a 6’×1/8’ SS packed adsorption column with a molecular sieve to identify carbon dioxide, carbon monoxide, and methane. The bottom product was distilled using a Koehler Model K 45090 and its physical properties were characterized, including the density (ASTM D86 using Stadbinger Densitometer), viscosity (ASTM D7042-04 using Viscometer SVM 3000), and cetane index. Fourier transform infrared spectroscopy (FT-IR) (Shimadzu) and gas chromatography/mass spectroscopy (GC-MS) were used to identify the functional groups and components in the hydrodeoxygenation product, respectively.

3. RESULTS AND DISCUSSION

3.1. Result of Catalyst Characterization

The goal of catalyst preparation is to produce a catalyst that is stable, active, and selective. To achieve this goal, the best preparative solution that affords sufficiently high surface area, good porosity, and suitable mechanical strength is needed. Table 1 shows the BET characterization result of NiMo/ZAL, where the pore volume of NiMo/ZAL is greater than that of the unactivated natural zeolite-Lampung. In the catalysis reaction, a large volume is needed to achieve a complete reaction, as the pore volume is the site of the reaction medium and can be considered a mini reactor. Furthermore, Table 1 shows the differences in the area of ZAL before and after NiMo is embedded. ZAL has a very large area before NiMo is embedded, and this area slowly decreases after NiMo enters the ZAL pores.

Table 1 Testing result of NiMo/ZAL catalyst using BET

Catalyst	Surface Area (m^2/g)	Pore Size (Å)	Pore Volume (cm^3/g)
ZAL	51.9	10.53	0.0045
NiMo/ZAL	12.25	9.83	0.0062

Figure 1 shows that the NiMo/ZAL catalyst still forms clots owing to the number of single particles. Vere few single particles were dispersed on the surface. This shows that the catalyst obtained had a different size.

Figure 1 Catalyst morphology of NiMo/ZAL: 1,000× magnifications (left), 10,000× magnifications (right)

The core content of the active Ni, Mo, and other metals in the catalyst was identified using energy-dispersive X-ray spectroscopy (EDX). The test result shows that the average yield of the active Ni and Mo contents in the catalyst was 5.96 wt% and 17.67 wt%, respectively. This value is similar to the number of active nuclei added during preparation.

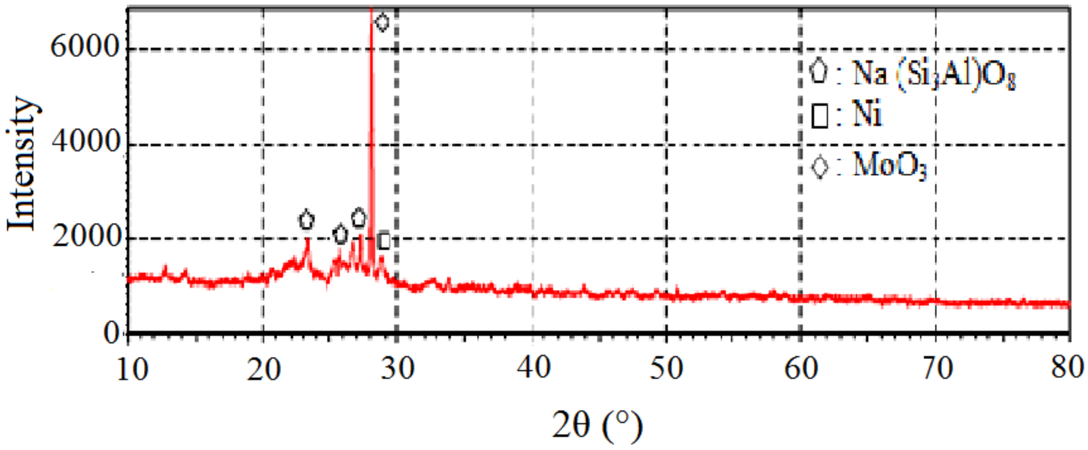

Figure 2 Diffractogram of NiMo/ZAL

Figure 2 shows the XRD pattern of NiMo/ZAL synthesized by the rapid cooling method. The peaks that appear in the catalyst show the same 2θ values. The peak that appears first corresponds to the top constituent ZAL component: $Na(Si_3Al)O_8$ at 2θ = 21.66° and cristobalite and albite structures at 2θ = 22.42°.

XRD shows that the NiMo/ZAL formed is crystalline. The crystal diffractogram of NiMo/ZAL shows a narrow peak. It indicates that the well-formed ZAL, Mo, and Ni metal crystals in the NiMo/ZAL catalyst are crystalline. The size of the NiMo particle supported on ZAL as estimated by the Debye–Scherrer formula is 70.07 nm.

3.2. Synthesis of Renewable Diesel through Hydrodeoxygenation

The activity catalyst test with the hydrodeoxygenation of palm oil and Jatropha curcas oil consisted of two main phases: activation of the catalyst and hydrodeoxygenation reaction. The catalyst was activated to improve the selectivity of the reaction. Hydrodeoxygenation was conducted after the catalyst was activated and the reactor temperature reached 100°C. The bottom product of the hydrodeoxygenation of palm oil and Jatropha curcas oil was still in the mixture, and it had to be purified by distillation. Distillation was performed at temperatures in the range of ~200°C initial boiling point (IBP 200), 200–300°C, and 300°C end point (EP 300). The distillation products at 300 EP were examined to determine the physical and chemical properties of the renewable diesel products. In this study, we use initial RD1 and RD2 for renewable diesel synthesized through the hydrodeoxygenation of palm oil and Jatropha curcas oil over NiMo/ZAL at 375°C and H_2 pressure of 15 bar.

3.2.1. Density of renewable diesel

Figure 3 shows that the density of RD1 and RD2 is less than that of conventional biodiesel (Boyás et al., 2008) and slightly higher than the minimum density of commercial diesel. This indicates that cracking and hydrodeoxygenation reactions occur over the NiMo/ZAL catalyst. RD1 has better density than RD2 and meets the specifications of commercial diesel.

3.2.2. Viscosity of renewable diesel

Palm oil and Jatropha curcas oil used as reactants in the synthesis of renewable diesel have very high viscosity before hydrodeoxygenation. Figure 4 shows that the viscosity of RD1 (32 cSt) and RD2 (52.76 cSt) decreased after hydrodeoxygenation. This was caused by the carboxylate bonding termination of palm oil and Jatropha curcas oil containing carbonyl (-CO) and hydroxyl (-OH) groups. The hydroxyl group in the carboxylic bond can form a hydrogen bond with the carbonyl group (CO), leading to a stronger bond between the molecules.

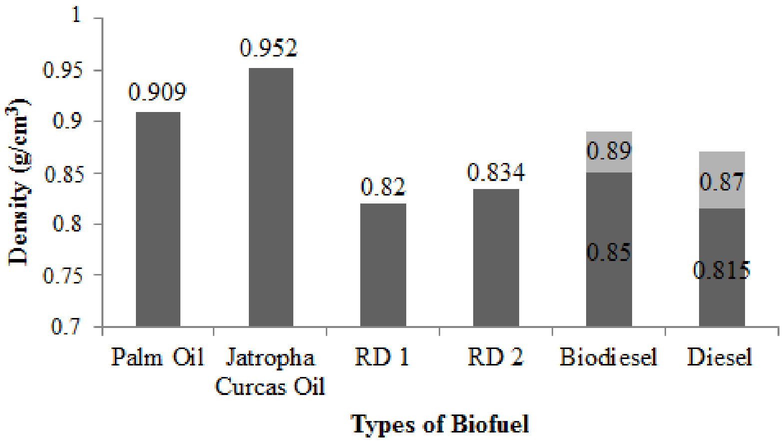

Figure 3 Comparison of density: palm oil, Jatropha curcas oil, renewable diesel, biodiesel, and diesel

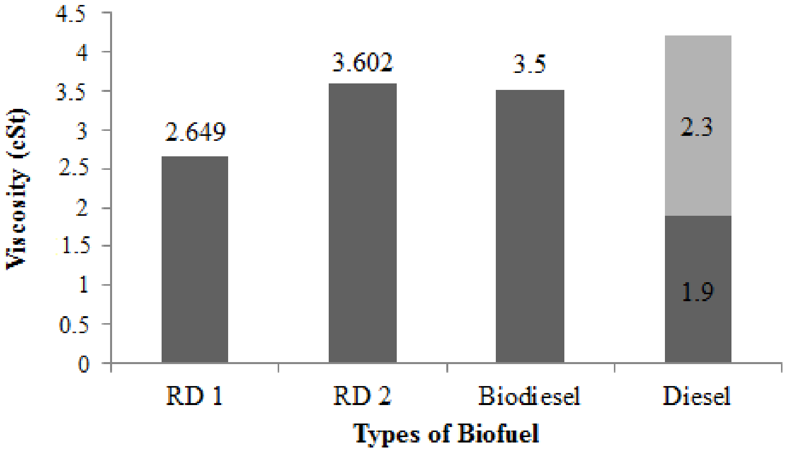

Figure 4 Comparison of viscosity: renewable diesel, biodiesel, and diesel

The viscosity of the renewable diesel products (RD1 and RD2), 1.9–4.1 cSt, meets the specification of standard diesel derived from fossils, namely, ASTM D-975. RD1 has better viscosity than RD2 and meets the specifications of commercial diesel. In addition, the viscosity of the renewable diesel product is much better than that of biodiesel based on the EN 14214 standard with minimum viscosity 3.5 cSt. As with the density analysis above, the use of NiMo/ZAL catalyst at 375°C and H_2 pressure of 15 bar is the optimum condition to obtain a renewable diesel product with viscosity similar to that of commercial diesel.

3.2.3. Cetane index of renewable diesel

The cetane index was measured to estimate the cetane number of the fuel. The cetane index was strongly influenced by the density and vapor temperature of renewable diesel as read using a thermocouple. The cetane index does not change if some additive with some cetane number is added to the fuel. The cetane index determines the combustion quality, emissions, and ability of the fuel to combust at low temperatures. Figure 5 shows the measured cetane index values.

Figure 5 shows that the cetane index values of RD1 and RD2 meet the minimum cetane index of diesel fuel (ASTM-D975). RD1 has a higher cetane index than RD2 and meets the specifications of commercial diesel. In general, the products of renewable diesel over NiMo/ZAL at a hydrodeoxygenation reaction temperature of 375°C and H_2 pressure of 15 bar have very suitable cetane index values that are much higher than that of diesel.

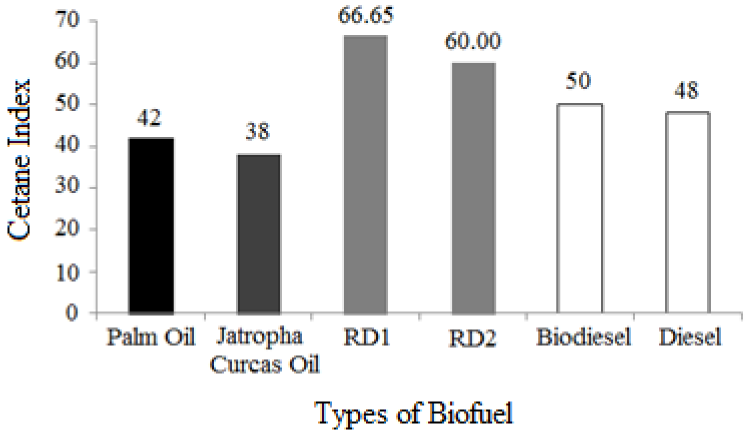

Figure 5 Comparison of cetane index: palm oil, Jatropha curcas oil, renewable diesel, biodiesel, and diesel

3.2.4. *Identification of bottom product using GC-MS*

Table 2 shows that the liquid bottom product consists of hydrocarbon fractions (C_1-C_{25}) and oxygenates such as acetone, alcohol, aldehyde, and carboxylic acid. The average mass percentage of the hydrocarbon fraction was above 50% and was more dominant than that of the oxygenate fraction. The C_{13}-C_{19} fraction was the primary hydrocarbon fraction contained in the bottom product. The remaining oxygenate fraction in the product could indicate the efficiency of the hydrodeoxygenation reaction.

Table 2 Total conversion, total hydrocarbon, total oxygenate, and total percentage of hydrocarbon fraction (selectivity and yield)

Product	**Conversion (%)**	**Selectivity (%)**				**Yield (%)**				**Total HC (%)**	**Total NonHC (%)**
		Biogasoline C_5-C_{11}	Biokerosine C_{11}-C_{13}	Renewable diesel C_{13}-C_{19}	Lubricants C_{19}-C_{25}	Biogasoline C_5-C_{11}	Biokerosine C_{11}-C_{13}	Renewable diesel C_{13}-C_{19}	Lubricants C_{19}-C_{25}		
RD1	80.87	7.16	8.47	52.78	5.01	6.19	7.33	45.66	4.33	63.51	36.49
RD2	79.04	4.68	7.87	47.12	2.13	4.05	6.81	40.76	1.84	53.46	46.54

The sample obtained by the hydrodeoxygenation of palm oil at 375°C and 15 bar over NiMo/ZAL produced the largest mass percentage of hydrocarbon (63.51%) and smallest percentage of nonhydrocarbon or oxygenate (36.49%). Hydrodeoxygenation produced a bottom liquid product, condensate, and gas. Table 2 shows that RD1 had the highest reactant conversion, selectivity, and yield of renewable diesel.

3.2.5. *Identification of gas product related to mechanism reaction*

Hydrodeoxygenation of palm oil and Jatropha curcas oil containing triglycerides is performed to remove oxygen and to saturate C=C double bonds to produce paraffinic n-alkanes in the boiling range of diesel. Hydrogen is reacted with the triglycerides under mild temperature and pressure in the presence of a catalyst to hydrogenate the double bonds in the fatty acid chains in the triglyceride. The glycerol backbone is broken and the oxygen is removed, leaving paraffinic n-alkanes (mostly n-C_{17} and n-C_{18} chains). There are three principal pathways by which oxygen can be removed from the triglycerides: hydrogenation, decarboxylation, and decarboxylation. These three pathways, shown in Figure 6, require different inputs and produce different products.

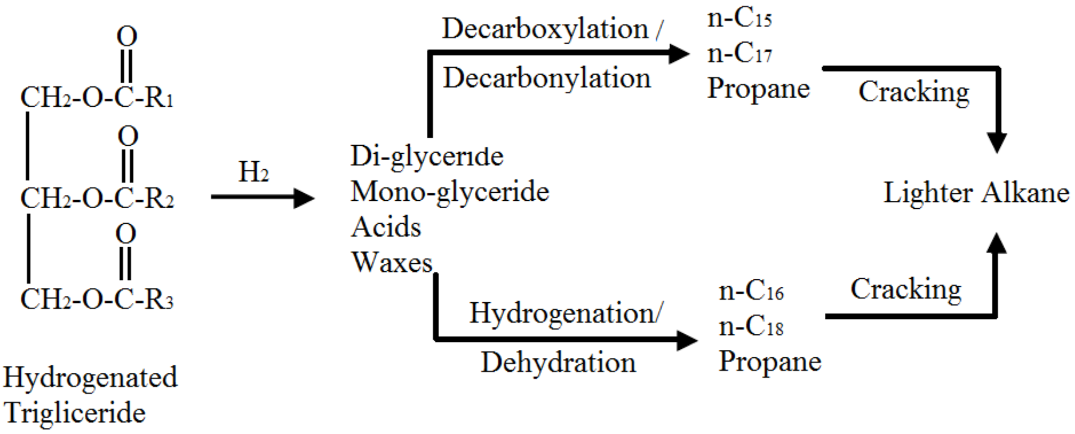

Figure 6 Synthesis route of hydrodeoxygenation of triglycerides to alkanes (Huber et al., 2007)

Under a temperature of 375°C and hydrogen pressure of 15 bar, vegetable oils such as palm oil and Jatropha curcas can be converted into paraffin (from n-C_{15} up to n-C_{18}), with water, propane, and CO_2 and CO gases produced as byproducts (Boyás et al., 2008). Intermediates such as monoglycerides, diglycerides, ketones, aldehydes, acrolein, and carboxylic acids are formed in the initial step and subsequently hydrogenated or broken down via decarboxylation, decarbonylation, or hydrodeoxygenation.

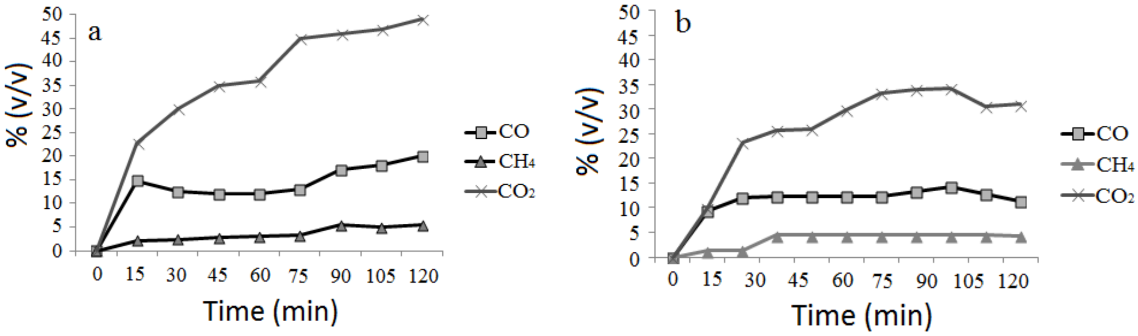

Figure 7 Gas rate formation curves: hydrodeoxygenation of: (a) palm oil; and (b) Jatropha curcas oil over NiMo/ZAL at 375°C and H_2 pressure of 15 bar

Figure 7 shows using NiMo/ZAL as a catalyst in the hydrodeoxygenation of palm oil and Jatropha curcas oil at a temperature of 375°C and H_2 pressure 15 bar had almost the same capabilities in directing the reaction path to decarboxylation (Boyás et al., 2008).

4. CONCLUSION

The following conclusions are derived from this study: NiMo/ZAL catalyst obtained by a rapid cooling method shows high crystallinity, with NiMo crystallite size of 70.07 nm, surface area of 12.25 m^2/g, and pore size and pore volume of 9.83 Å and 0.0062 cm^3/g, respectively; it also shows good catalytic activity. The renewable diesels obtained by the reaction show suitable density and viscosity and high cetane index at a temperature of 375°C and H_2 pressure of 15 bar. The triglycerides of palm oil and Jatropha curcas oil have similar structures, and therefore, they can be used as feedstock to produce renewable diesel through hydrodeoxygenation. The renewable diesels thus obtained have quality similar to conventional renewable diesel.

5. ACKNOWLEDGEMENT

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